

solution volume to 100 ml using additional water. Shake well to mix the solution.

7.1.6 Sodium Thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$)

7.2 Sample Preparation and Analysis.

7.2.1 Water. Same as in Section 7.1.2.

7.2.2 Absorbing Solution Blanks. A separate blank solution of each absorbing reagent should be prepared for analysis with the field samples. Dilute 30 ml of each absorbing solution to approximately the same final volume as the field samples using the blank sample of rinse water.

7.2.3 Halide Salt Stock Standard Solutions. Prepare concentrated stock solutions from reagent grade sodium chloride (NaCl), sodium bromide (NaBr), and sodium fluoride (NaF). Each must be dried at 110 °C (230 °F) for two or more hours and then cooled to room temperature in a desiccator immediately before weighing. Accurately weigh 1.6 to 1.7 g of the dried NaCl to within 0.1 mg, dissolve in water, and dilute to 1 liter. Calculate the exact Cl^- concentration using Equation 26-1 in Section 12.2. In a similar manner, accurately weigh and solubilize 1.2 to 1.3 g of dried NaBr and 2.2 to 2.3 g of NaF to make 1-liter solutions. Use Equations 26-2 and 26-3 in Section 12.2, to calculate the Br^- and F^- concentrations. Alternately, solutions containing a nominal certified concentration of 1000 mg/l NaCl are commercially available as convenient stock solutions from which standards can be made by appropriate volumetric dilution. Refrigerate the stock standard solutions and store no longer than one month.

7.2.4 Chromatographic Eluent. Effective eluents for nonsuppressed IC using a resin- or silica-based weak ion exchange column are a 4 mM potassium hydrogen phthalate solution, adjusted to pH 4.0 using a saturated sodium borate solution, and a 4 mM 4-hydroxy benzoate solution, adjusted to pH 8.6 using 1 N NaOH. An effective eluent for suppressed ion chromatography is a solution containing 3 mM sodium bicarbonate and 2.4 mM sodium carbonate. Other dilute solutions buffered to a similar pH and containing no interfering ions may be used. When using suppressed ion chromatography, if the "water dip" resulting from sample injection interferes with the chloride peak, use a 2 mM NaOH/2.4 mM sodium bicarbonate eluent.

7.3 Quality Assurance Audit Samples. When making compliance determinations, and upon availability, audit samples may be obtained from the appropriate EPA regional Office or from the responsible enforcement authority.

NOTE: The responsible enforcement authority should be notified at least 30 days prior to the test date to allow sufficient time for sample delivery.

8.0 Sample Collection, Preservation, Storage, and Transport

NOTE: Because of the complexity of this method, testers and analyst should be trained and experienced with the procedure to ensure reliable results.

8.1 Sampling.

8.1.1 Preparation of Collection Train. Prepare the sampling train as follows: Pour 15 ml of the acidic absorbing solution into each one of the first pair of impingers, and 15 ml of the alkaline absorbing solution into each one of the second pair of impingers. Connect the impingers in series with the knockout impinger first, if used, followed by the two impingers containing the acidic absorbing solution and the two impingers containing the alkaline absorbing solution. Place a fresh charge of silica gel, or equivalent, in the drying tube or impinger at the end of the impinger train.

8.1.2 Adjust the probe temperature and the temperature of the filter and the stopcock, *i.e.*, the heated area in Figure 26-1 to a temperature sufficient to prevent water condensation. This temperature should be at least 20 °C (68 °F) above the source temperature, and greater than 120 °C (248 °F). The temperature should be monitored throughout a sampling run to ensure that the desired temperature is maintained. It is important to maintain a temperature around the probe and filter of greater than 120 °C (248 °F) since it is extremely difficult to purge acid gases off these components. (These components are not quantitatively recovered and hence any collection of acid gases on these components would result in potential underreporting of these emission. The applicable subparts may specify alternative higher temperatures.)

8.1.3 Leak-Check Procedure.

8.1.3.1 Sampling Train. A leak-check prior to the sampling run is optional; however, a leak-check after the sampling run is mandatory. The leak-check procedure is as follows: Temporarily attach a suitable [*e.g.*, 0-40 cc/min (0-2.4 in³/min)] rotameter to the outlet of the dry gas meter and place a vacuum gauge at or near the probe inlet. Plug the probe inlet, pull a vacuum of at least 250 mm Hg (10 in. Hg), and note the flow rate as indicated by the rotameter. A leakage rate not in excess of 2 percent of the average sampling rate is acceptable.

NOTE: Carefully release the probe inlet plug before turning off the pump.

8.1.3.2 Pump. It is suggested (not mandatory) that the pump be leak-checked separately, either prior to or after the sampling run. If done prior to the sampling run, the pump leak-check shall precede the leak-check of the sampling train described immediately above; if done after the sampling run, the pump leak-check shall follow the train leak-check. To leak-check the pump, proceed as follows: Disconnect the drying tube from

the probe-impinger assembly. Place a vacuum gauge at the inlet to either the drying tube or pump, pull a vacuum of 250 mm (10 in) Hg, plug or pinch off the outlet of the flow meter, and then turn off the pump. The vacuum should remain stable for at least 30 sec. Other leak-check procedures may be used, subject to the approval of the Administrator, U.S. Environmental Protection Agency.

8.1.4 Purge Procedure. Immediately before sampling, connect the purge line to the stopcock, and turn the stopcock to permit the purge pump to purge the probe (see Figure 1A of Figure 26-1). Turn on the purge pump, and adjust the purge rate to 2 liters/min (0.07 ft³/min). Purge for at least 5 minutes before sampling.

8.1.5 Sample Collection. Turn on the sampling pump, pull a slight vacuum of approximately 25 mm Hg (1 in Hg) on the impinger train, and turn the stopcock to permit stack gas to be pulled through the impinger train (see Figure 1C of Figure 26-1). Adjust the sampling rate to 2 liters/min, as indicated by the rate meter, and maintain this rate to within 10 percent during the entire sampling run. Take readings of the dry gas meter volume and temperature, rate meter, and vacuum gauge at least once every five minutes during the run. A sampling time of one hour is recommended. Shorter sampling times may introduce a significant negative bias in the HCl concentration. At the conclusion of the sampling run, remove the train from the stack, cool, and perform a leak-check as described in Section 8.1.3.1.

8.2 Sample Recovery.

8.2.1 Disconnect the impingers after sampling. Quantitatively transfer the contents of the acid impingers and the knockout impinger, if used, to a leak-free storage bottle. Add the water rinses of each of these

impingers and connecting glassware to the storage bottle.

8.2.2 Repeat this procedure for the alkaline impingers and connecting glassware using a separate storage bottle. Add 25 mg of sodium thiosulfate per the product of ppm of halogen anticipated to be in the stack gas times the volume (dscm) of stack gas sampled (0.7 mg per ppm-dscf).

NOTE: This amount of sodium thiosulfate includes a safety factor of approximately 5 to assure complete reaction with the hypohalous acid to form a second Cl⁻ ion in the alkaline solution.

8.2.3 Save portions of the absorbing reagents (0.1 N H₂SO₄ and 0.1 N NaOH) equivalent to the amount used in the sampling train (these are the absorbing solution blanks described in Section 7.2.2); dilute to the approximate volume of the corresponding samples using rinse water directly from the wash bottle being used. Add the same amount of sodium thiosulfate solution to the 0.1 N NaOH absorbing solution blank. Also, save a portion of the rinse water used to rinse the sampling train. Place each in a separate, prelabeled storage bottle. The sample storage bottles should be sealed, shaken to mix, and labeled. Mark the fluid level.

8.3 Sample Preparation for Analysis. Note the liquid levels in the storage bottles and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Quantitatively transfer the sample solutions to 100-ml volumetric flasks, and dilute to 100 ml with water.

9.0 Quality Control

Section	Quality control measure	Effect
11.2	Audit sample analysis	Evaluate analytical technique, preparation of standards.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory log of all calibrations.

10.1 Volume Metering System, Temperature Sensors, Rate Meter, and Barometer. Same as in Method 6, Sections 10.1, 10.2, 10.3, and 10.4.

10.2 Ion Chromatograph.

10.2.1 To prepare the calibration standards, dilute given amounts (1.0 ml or greater) of the stock standard solutions to convenient volumes, using 0.1 N H₂SO₄ or 0.1 N NaOH, as appropriate. Prepare at least four calibration standards for each absorbing reagent containing the appropriate stock solu-

tions such that they are within the linear range of the field samples.

10.2.2 Using one of the standards in each series, ensure adequate baseline separation for the peaks of interest.

10.2.3 Inject the appropriate series of calibration standards, starting with the lowest concentration standard first both before and after injection of the quality control check sample, reagent blanks, and field samples. This allows compensation for any instrument drift occurring during sample analysis. The values from duplicate injections of these calibration samples should agree within 5 percent of their mean for the analysis to be valid.